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(21) International Application Number: PCT/US99/30790 (22) International Filing Date: 22 December 1999 (22.12.99) (30) Priority Data: 09/223,664 30 December 1998 (30.12.98) US (71) Applicant: THE B.F. GOODRICH COMPANY [US/US]; 4020 Kinross Lakes Parkway, Richfield, OH 44286 (US). (72) Inventors: GALLEGUILLOS, Ramiro; 5645 Williamsburg Circle, Hudson, OH 44236 (US). SMITH, David, J.; 613 Winesap Road, Amherst, OH 44001 (US). CON- STANTINO, Steven, P.; 14623 LaGrange Road, LaGrange, OH 44050 (US). (74) Agents: HUDAK, Daniel, J.; Hudak & Shunk Co., L.P.A., Suite 808, 7 West Bowery Street, Akron, OH 44308-1133 (US) et al.	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: BRANCHED/BLOCK COPOLYMERS FOR TREATMENT OF KERATINOUS SUBSTRATES (57) Abstract A block copolymer for hair styling compositions includes hydrophilic and hydrophobic blocks which allow for optimization of desirable characteristics of the hair styling composition, such as style retention at high humidity, tack, hardness, resistance to flaking, and washability from the hair. The copolymer includes a polyacrylate backbone of hydrophobic blocks, with hydrophilic acrylate side chains. The copolymer is suitable for the formulation of a number personal care, household, hair care, skin-care and other formulation. The copolymer is suited to incorporation into low VOC hydra-alcoholic hair styling compositions to meet reduced VOC, regulations.		

unsaturated monomer(s) to form an A-Block, and then polymerizing a second ethylenically unsaturated monomer(s) containing at least one carboxylic acid group with the A-block to form a B-block and a copolymer having hydrophobic and hydrophilic blocks. To prepare hair styling compositions 1-20 % wt. of the block copolymer is
5 combined with 20-97 % wt. of water, 0 to 80 % wt. of organic solvent, 0 to 5 % wt. surfactant and conditioning agents, 0 to 1% wt. fragrance, and other ancillary agents.

One advantage of the present invention is that it enables hair styling compositions to be prepared with optimal performance properties, such as style retention at high humidity, tack, hardness, flaking, washability from the hair and other subjective
10 performance attributes.

Another advantage of the present invention is that the copolymers provided can be incorporated into hydro-alcoholic hair styling formulations to meet reduced VOC, regulations and they are effective as styling agents in a wide variety of hair styling formulations, including aerosol sprays, mousses, spritzes, gels, setting
15 lotions, and the like.

Yet another advantage of the present invention is that the copolymers can be used for a variety of other applications where a coating composition or film forming polymer would be employed which can benefit from the fact that the block copolymer has hydrophobic and hydrophilic blocks.

20

Detailed Description of the Preferred Embodiments

A-Block/branched copolymer having two or more distinct glass transition temperatures (T_g) can be tailored to provide the desired properties in a hair care composition. The copolymer has a block structure, consisting essentially of a hard, hydrophilic block, which contributes to a high T_g , and a soft, more hydrophobic block, which contributes to a low T_g . The hydrophobic block forms the A-Block of the
25 copolymer, while the hydrophilic block forms the B-Block. The hydrophilic B-Block and hydrophobic A-Block contribute different properties to the overall copolymer. The soft, low- T_g hydrophobic A-Block contributes properties such as the formation of a uniform, clear film on the surface of the hair, providing high humidity resistance for durable hair style retention, conditioning and detangling the hair while wet, conferring
30 the dried hair with a soft feel to the touch, adherence to the hair without flaking,

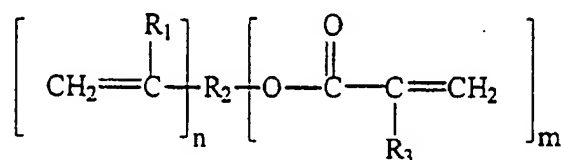
where A represents the monomer or monomers of the first block, referred to herein as the "A-Block," and B represents the monomer or monomers of the second block, referred to herein as the "B-Block." X represents a chain branching agent or a multifunctional monomer used to link the A and B-Blocks. In these structures, n represents the degree of polymerization of the A-Block, i.e., the number of monomer units in the A-Block. Its value is typically larger than 100. The letters q and p represent the degree of polymerization of the B-Block, i.e. the number of monomer units in the B-Block. Their added value is typically larger than 100. Either q or p can take the value of zero but not both at the same time. The straight line between two monomers (A—A) represents a covalent chemical bond.

The copolymers of this invention, as represented in Structures 1 and 2 above, are blocky and may form three-dimensional networks. The existence of the two blocks was confirmed by conducting differential scanning calorimetry on dry polymer samples. It is well known that the presence of two or more transition temperatures, T_g 's, is a clear indication of the blocky character of the copolymers, see. e.g., "Contemporary Polymer Chemistry" 2nd. Edition by H. Allcock and F. Lampe, Ch. 17, Prentice Hall Publishers, 1990. The A-Blocks and the B-Blocks are covalently or chemically attached through the chain branching agent X.

The average molecular weight of the copolymer can reach up to 1,000,000. The preferred molecular weight is in the 20,000 to 250,000 range. The preferred molecular weight of the A-Block is in the range of 10,000 to 150,000, whereas the preferred molecular weight of the B-Block is in the range of 1,000 to 50,000.

Therefore, the copolymers of this invention attain their unique hair styling and fixing properties attributes due to a combination of soft and hard blocks. The A-Block is a soft more hydrophobic block, with low T_g , and the B-Block is a hard, hydrophilic high T_g block. In addition, the length and composition of the blocks of the polymer can be varied to improve specific performance needs. In particular, the copolymers of this invention are designed to provide long lasting hair style retention at high humidity, natural feel, good hair combing, reduced flaking, no build up, and good hair styling and restyling. They are good film formers, water and alcohol soluble or dispersible and washable with water and shampoo.

The structure of the chain branching agent can be of the following type:



5 where $n, m = 1$ to $4, m + n \geq 2$

$\text{R}_1, \text{R}_3 = \text{H, Alkyl}$

$\text{R}_2 = \text{alkyl, cycloalkyl, aryl,}$

$-(\text{CH}_2-\text{CH}_2-\text{O})_p-$ where $p = 1$ to $50,$

$-(\text{CH}_2(\text{CH}_3)-\text{CH}_2-\text{O})_p-$ where $p = 1$ to $50,$

10 amido, ester, polyamido, polyester.

The reactivity of one of the functional groups should be relatively lower than the reactivity of the other. Table 1 below shows the reactivity ratios, r_1 and r_2 , for allyl, acrylic and methacrylic functional groups; as defined in the Polymer Handbook, by H. Immergut and J. Brandrup, 3rd Edition, Interscience, 1989. It can be seen that the allyl groups react 3 to 10 times slower than the other groups.

Table 1 Reactivities of Functional Groups

Fast Monomer/Slow Monomer	r_1	r_2
Acrylic Acid/Allyl Acetate	0.500	0.061
Methacrylic Acid/Allyl Acetate	1.129	0.066
Ethyl Acrylate/Allyl Acetate	0.600	0.165
Methyl Methacrylate/Allyl Acetate	0.383	0.136
n-Butyl acrylate/Allyl Acetate	0.427	0.199

20 Other multifunctional branching agents can also be used. Their selection should be based on the relative reactivity of their polymerizable groups. If the reactivity of the functional groups is substantially similar, then gelation during polymerization tends to occur. The polymer form is then difficult to remove from the reactor.

The monomers B are hydrophilic, or water-soluble monomers which are sufficiently water soluble to form at least a ten-weight percent solution when dissolved in

If monomers **B** are acidic, they make it possible for the resultant copolymer to be neutralized by reaction with an appropriate base so that the copolymer may exhibit a desirable level of water solubility. For example, the copolymer may be neutralized prior to being incorporated into an ultimate hair styling composition, allowing the composition to be removed from the hair simply by washing with water. Alternatively, if the copolymers are not pre-neutralized in this manner, removal may still be readily effected by application of an aqueous alkaline solution, such as soap in water.

The exact ratio of the monomers **A** and **B** is not critical to solubility. Copolymers with a high proportion of the hydrophobic **A-Block** can be dissolved in water by adjusting the pH.

In order to modify or enhance selected properties of the copolymer, for example, resistance to humidity, washability, and the like, the monomers **A** and **B** may be single monomers, or a combination of two or more monomers.

As for the actual preparation of the copolymer, any of the usual acrylate polymerization methods known in the art, such as solvent, suspension, emulsion, and inverse emulsion polymerization methods may be employed. In one preferred method of preparation of the copolymer, the monomers **A**, **B**, and **X** are reacted together in a suitable solvent. A free radical initiator is added in small quantities.

Suitable free radical initiators include azo- and peroxy-type initiators. Examples of azo-initiators are azobis-dimethylvaleronitrile, azobis-isobutyronitrile, azobis-methylbutyronitrile and others sold by DuPont, Wilmington, DE under the trade name VAZO and by WAKO Pure Chemical Industries, Richmond, VA under the trade name of V-40 to V501. Examples of peroxy initiators include di-T butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxyphthalate, lauryl peroxide, cumene hydroperoxide, ethyl hexyl peroxodicarbonate, diisopropyl peroxydicarbonate, 4-(t-butylperoxycarbonyl)-3-hexyl-6-7-(t-butylperoxycarbonyl)heptyl cyclohexene (4-TBPCH), cumene hydroperoxide and t-butyl peroxyneodecanoate, t-butyl hydroperoxide, benzoyl peroxide and other organic peroxides sold by Elf Atochem North America, Inc., Philadelphia, PA, under the trade names of Lupersol, Luperco, Lucidol and Luperox.

The initiator is preferably added at about 0.005 mole percent to 1 mole percent of the total monomer composition. Preferred initiators are di-T-butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxyphthalate, lauryl peroxide, cumene hydroperoxide,

allyl methacrylate, were mixed together and charged into a storage cylinder connected to the reactor by a feed line and a metering pump. 16.8 grams of an initiator, t-butyl peroxyvalate were diluted with a further 200 grams of solvent and charged to another storage cylinder also connected to the reactor by a metering pump.

5 After the reactor reached reflux temperature the polymerization was started. The first batch of monomers was fed in evenly over a one hour period and the initiator was fed in over evenly over a four hour period. After the first hour, a second batch, or feed, of monomers for forming the B-Block, a blend of 1053 grams of methacrylic acid and 10 grams of allyl methacrylate chain extender was fed into the reactor evenly over a two
10 hour period. The total monomer feed time was three hours and the total initiator feed time was four hours. After all the ingredients had been added, the reactor was held at reflux temperature for another two hours before cooling to room temperature.

 The resulting reaction mixture comprised 50 percent solids by weight.

 The above method was used to prepare copolymers of varying
15 compositions. The molecular weight (Mw) of the polymers was measured by gel permeation chromatography, GPC. The T_g of the polymers was measured using differential scanning calorimetry, DSC. Table 2 summarizes the quantities of the three monomers used in preparing each of the copolymers, in terms of the weight added in each of the two feed mixtures, and the total weight of monomer added in both the
20 mixtures. The percentage solids in the reactor at the end of the reaction period is included for each of the copolymers prepared, together with the high and low glass transition temperatures of the copolymer, and the molecular weight of the copolymer.

Key for the Examples of Polymers:

25 In the examples, the following abbreviations will be used:

nBA = n-butyl acrylate

All MA = (chain extender) allyl methacrylate

AA = acrylic acid

30 MAA = methacrylic acid

EGDMA = (chain extender) ethylene glycol dimethacrylate

Lup-11 = (initiator) t-butyl peroxyvalate (Lup-11 is short for Lupersol-11, and is available from Atochem North America, Inc.)

TABLE 5

(Subjective properties were evaluated directly on hair tresses. 1= worst, 10= best)

Polymer	Hair Feel	Tack	Flake off	Sprayability	% Set Retention 1 hr, 90% RH
PVP, *	3	2	2	1	30.00
Amphomer **	2	3	8	2	80.00
Lovocryl L73 ***	2	3	8	2	50.00
Luv VA73	4	6	6	3	30.00
Luv Hold.	4	6	6	3	30.00
Example 7	6	5	8	6	30.00
Example 8	6	5	8	8	90.00
Example 9	5	5	8	7	84.00
Example 10	5	5	3	3	100.00

* PVP is polyvinyl pyrrolidone

** Amphomer is a polymer sold by the M.H. Starch Co.

*** Lovocryl, Luv are trade names for polymers sold by BASF

An important performance property that a hair fixative polymer must also have, is its ability to hold a hairstyle in place at relatively high humidity, i.e., Curl Retention. The curl retention ability of the copolymers of this invention was measured and compared against a number of current hair fixative polymers.

Curl Retention Protocol: 0.05 grams of resin dissolved in a hydroalcoholic solution was applied and smeared on clean, 2 grams, 6 in. hair swatches. The swatches were rolled over salon rollers, dried and conditioned overnight. The swatches were mounted inside a humidity chamber at 80°F, and 90 % of relative humidity.

The curl retention was recorded as a function of time and calculated as:

$$L-L(t)/L-L(o) \times 100 = \text{curl retention \%}$$

Where:

L=length of hair fully extended, L(o)=length of hair before exposure to high humidity,
L(t)=length of hair after exposure at time(t).

As shown in Table 5, the curl retention ability of the blocky-branched copolymers of Examples 8, 9, and 10 was superior to most current fixative polymers.

Copolymer examples 11 and 12, in Table 6, show block copolymers where the A-Block includes 2 ethylhexacrylate (2-EHA) and ethylacrylate (EA), respectively.

TABLE 6

Example	Monomer Composition				Observations
	Ingredients	A-Block (g)	B-Block (g)	Total Batch (g) (phm)	
11	MAA	446.00		1316.50	<i>Soluble in water at pH = 8.02</i>
	2-EHA	1200.00		1200.00	
	All MA	25.00	12.50	37.50	
	Lup-11			30.00	
	IPA/H ₂ O			3000.00	
12	MAA	446.00	1316.50	1762.50	<i>Soluble in water at pH = 6.61</i>
	EA	1200.00		1200.00	
	All MA	25.00	12.50	37.50	
	Lup-11			21.00	
	IPA/H ₂ O			3000.00	

Low VOC hair styling compositions were prepared using the copolymers of Example 2. The compositions included 3-5 weight percent of a resin containing 60% weight percent of one of the copolymers of Table 2, a solvent system, comprising ethanol and water, and a surfactant, AMP-95. All the compositions were formulated to 50% by weight VOC's. Table 7 lists the components of compositions and summarizes the subjective assessments. The compositions show improved performance over conventional, widely used hair styling formulations. The improved performance is seen in one or more of the following attributes: style retention at high humidity, natural feel, combability, reduced flaking, good styleability and restyleability.

TABLE 7: Hair Styling Compositions Containing 50% VOC

Composition A

Ingredient	% wt	Comments:
Polymer of Example 1	3.00	Feel of hair is slick initially then it has a very touchable feel when completely dry.
Ethanol	50.00	
Amp 95 *	0.30	
Deionized water	46.70	

* AMP 95 is amino methyl propanol, 95% wt. in water

Composition B

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 2	5.00	Same as for composition A.
Ethanol	50.00	
Amp 95	0.50	
Deionized water	44.50	

Composition C

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 3	3.00	Feel of hair is slick initially then becomes touchable when dry. Humidity resistance is greater than for conventional PVP and PVP/vinyl acetate in alcohol formulations.
Ethanol	50.00	
Amp 95	0.17	
Deionized water	46.83	

5

Composition D

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 3	5.00	Same as for Composition C.
Ethanol	50.00	
Amp 95	0.29	
Deionized water	44.71	

10

Swatches of hair were sprayed or applied with the hair styling compositions in Table 7. The swatches were evaluated for humidity resistance, expressed in terms of percentage droop (in relation to a fully extended swatch of hair). Subjective assessments of natural feel, combability, resistance to flaking, and restylability/stylability were also made, on a 1 to 10 scale, 10 being the optimum. Table 8 summarizes these characteristics for the four hair styling compositions in Table 7.

TABLE 8. Hair Styling Properties of Compositions Including the Copolymer

<u>Composition</u>	<u>Humidity Resistance</u>	<u>Natural Feel</u>	<u>Combability</u>	<u>Flaking</u>	<u>Restylability Stylability</u>
A	30 min - 76% curl drop. 45 min - curl drop	6	9	8	7
B	30 min - 92% curl drop. 1 hr. - curl drop	6	9	7	7
C	7 hrs. - 88% curl drop, 24 hrs. - full droop	6	9	10	8
D	46 hrs - 88% curl drop, 72 hrs. - full droop	6	9	8	8

15

Example G. Styling Mousse

	<u>Item No.</u>	<u>Ingredient</u>	<u>Wt %</u>
	1	Water	81.0
5	2	Polymer of Example 5	3.5
	3	Emulphor on-870	0.5
	4	Propellant A-46	15.0

Item 1 thru 3 were added and mixed in a container until a clear solution is obtained. This
 10 formulation was placed in an aerosol mousse can. The can was capped with a standard
 mousse actuator. Item 4 was pressure charged into the can. Upon discharging the
 product, a thick and creamy foam was obtained.

The following examples are intended to illustrate the range of uses for the
 15 film forming copolymers of this invention:

Ultrasonic Diagnosis Gel

0.5% Carbomer thickener
 2.0% Polymer of Example 7
 0.25% of NaOH
 20 5.0% of glycerol to 100% with water + preservative

Ointment with Zinc Oxide

1.2% Polymer of Example 10
 1.0% triethanolamine
 25 14.0% of zinc oxide to 100% with water + preservative

Furniture Polish

1.0% Polymer of Example 10
 5.0% silicone oil emulsions (30% strength)
 30 3.0% carnauba wax emulsion (20% strength) to 100% with water

Domestic Cleaning Agent

1.5% Polymer of Example 10
 1.3% triethanolamine
 35 10.0% isopropyl alcohol
 10.0% nonylphenol + 10 moles of ethylene oxide to 100% water

Water-In-Oil Cream

- 5 0.5% Polymer of Example 10
0.1% monoethanolamine
3.5% diglycerol sesquiisostearate
10.0% paraffin wax
5.0% cetyl alcohol
2.2% microwax
0.2% perfume oil to 100% water + perservative

10 After Shave Gel

- 1.1% Polymer of Example 10
0.4% monoethanolamine
35.0% ethyl alcohol
0.1% menthol to 100% with water + preservative

15

Hair Shampoo

- 0.5% Polymer of Example 10
0.6% triethanolamine
12.0% coconut oil alcohol + 10 moles of ethylene oxide
20 0.1% perfume oil to 100% of water + preservative

Hand Sanitizer

- 1.0% Polymer of Example 10
65.0% ethyl alcohol
25 1.5% carbopol
1.4% triethanolamine
0.1% perfume oil to 100% with water + preservative

Liquid Oil-In-Water Emulsion

- 30 0.5% Polymer of Example 10
0.2% NaOH
5.0% isopropyl palmitate
5.0% paraffin oil
5.1% diglycerol stearate + 4 moles of ethylene oxide
35 0.1% perfume oil to 100% with water + preservative

Oil-In-Water Cream

- 0.7% Polymer of Example 10
0.6% AMP-95
40 5.0% petrolatum
5.2% soybean oil
3.0% glycerol monostearate
3.0% tri-stearyl tetraglycol ether ortho-phosphoric acid to 100% with water +
45 preservative

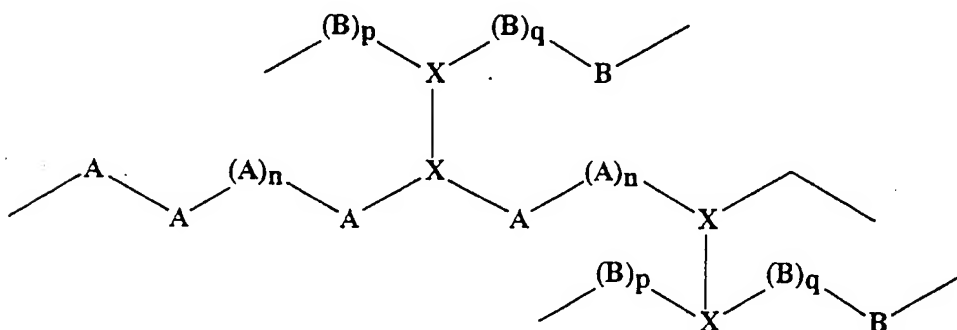
Liquid Water-In-Oil Emulsion

- 0.5% Polymer of Example 10
- 0.6% ammonium hydroxide (10% strength)
- 3.0% hydrogenated castor oil + 7 moles of ethylene oxide
- 5 2.0% polyglyceryl-2 sesquiisostearate
- 1.0% beeswax
- 1.0% mineral oil
- 0.5% magnesium stearate
- 0.5% aluminum montanate
- 10 10.0% isopropyl palmitate
- 15.0% perhydrosqualene to 100% with preservative + water

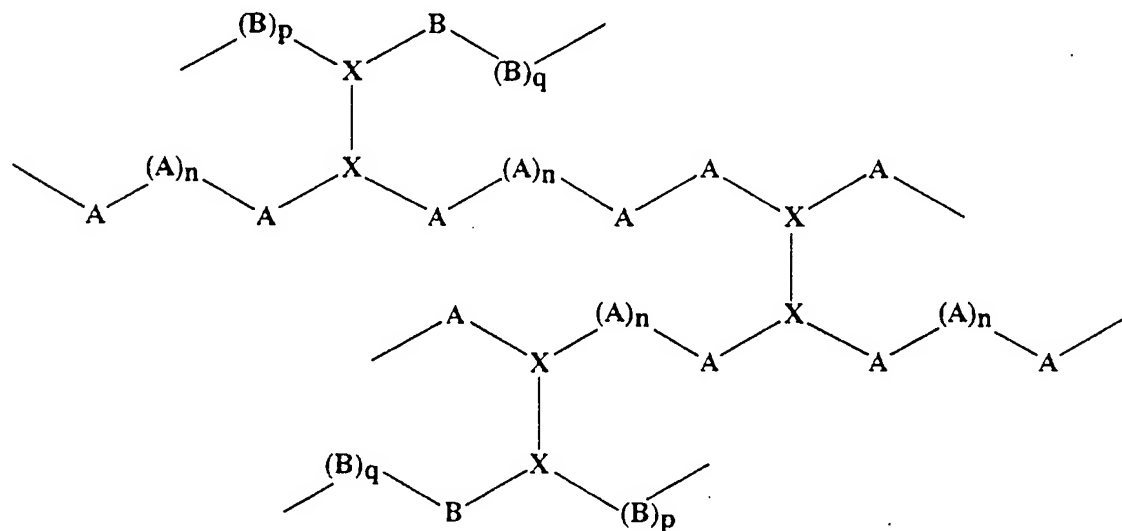
The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

Having thus described the preferred embodiment, the invention is now claimed to be:

1. A film forming block copolymer having a structure selected from the group consisting of the following :



Structure 1.



Structure 2.

wherein A represents the monomer or monomers of a first block, B represents the monomer or monomers of a second block, X represents the extender monomer, n is the degree of polymerization of the A-Block, q and p represent the degree of polymerization

of the B-Block, and either q or p can take the value of zero but not both at the same time, both the A block and the B block are derived from ethylenically unsaturated monomers, the A block is more hydrophobic than the B block, and the copolymer has at least two different glass transition temperatures.

5

2. A film forming block copolymer for application to keratinous substrates which has been prepared by polymerizing:

a polyfunctional monomer or monomers, having at least two functional groups, the reactivity of one functional group being higher than that of other functional group;

10

a first ethylenically unsaturated monomer or monomers which copolymerize preferentially with the functional group of the difunctional monomer which has a higher functionality to form a first block; and

a second ethylenically unsaturated monomer or monomers, which contains at least one carboxylic acid group and copolymerizes with the functional group of the difunctional monomer which has the lesser functionality to form a second block, wherein the first block is more hydrophobic than the second block. and the copolymer has both hydrophobic and hydrophilic blocks, which have at least two different glass transition temperatures.

15
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3. The copolymer of claim 2, wherein:

the polyfunctional monomer comprises from about 0.005 to 2 mole percent of the total monomers;

the first ethylenically unsaturated monomer comprises from about 5 to about 95 mole percent of the total monomers; and,

25

the second ethylenically unsaturated monomer comprises from about 5 to about 70 mole percent of the total monomers.

4. The copolymer of claim 2, wherein:

the polyfunctional monomer comprises from 0.1 to 1.5 mole percent of the total monomers;

30

the first ethylenically unsaturated monomer comprises from 5 to 50 mole percent of the total monomers; and,

the second ethylenically unsaturated monomer comprises from 10 to 70 mole percent of the monomers.

5

5. The copolymer of claim 2, wherein the copolymer has a molecular weight of less than 1, 000,000.

10

6. The copolymer of claim 2, wherein the first block has a molecular weight of 10,000 to 100,000.

7. The copolymer of claim 2, wherein the second block has a molecular weight of 1,000 to 100,000.

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8. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of monomers having at least 2 to 30 carbon atoms.

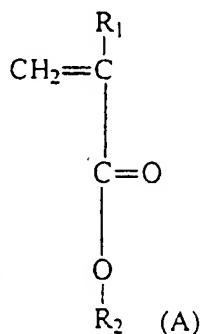
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9. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of:

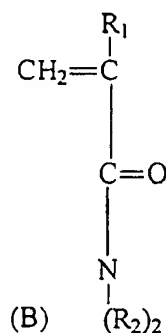
acrylate and methacrylate esters and acids;

N-substituted acrylamides, substituted with alkyl radicals containing from 2 to 12 carbon atoms; and,

esters having the general formula:



or



25

where R₁ is selected from the group consisting of -H, -CH₃,
-CH₂CH₃; and,

R₂ is an aliphatic hydrocarbon functional group having at least two
carbons, such as C₁ to C₂₀ alkyls and cycloalkyls; polynuclear aromatic hydrocarbon
5 groups such as naphthyls; alkylaryls wherein the alkyl has one or more carbons,
preferably 4 to 8 carbons; haloalkyls of 4 or more carbons, such as perfluoroalkyls;
polyalkyleneoxy groups wherein alkylene is propylene or higher alkylene and there is at
least 1 alkyleneoxy unit per hydrophobic moiety; and combinations thereof.

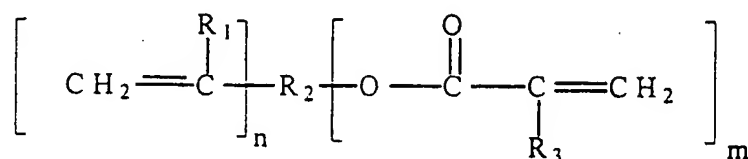
10 10. The copolymer of claim 2, wherein the first ethylenically
unsaturated monomer is selected from the group consisting of the higher alkyl esters of
α,β-ethylenically unsaturated carboxylic acids; ethyl half ester of maleic anhydride;
diethyl maleate; alkyl esters derived from the reactions of alkanols having from 2 to 20
carbon atoms with ethylenically unsaturated carboxylic acids; alkylaryl esters of
15 ethylenically unsaturated carboxylic acids; N-alkyl, ethylenically unsaturated amides;
α-olefins; vinyl alkylates wherein the alkyl has at least 8 carbons; vinyl alkyl ethers;
N-vinyl amides; and ar-alkylstyrenes; and combinations thereof.

20 11. The copolymer of claim 2, wherein the first ethylenically
unsaturated monomer is an acrylamide or methacrylamide selected from the group
consisting of N-ethyl acrylamide, N-tertiary-octyl acrylamide, N-decyl acrylamide, N-
dodecyl acrylamide, N-ethyl methacrylamide, N-tertiary octyl methacrylamide, N-decyl
methacrylamide, N-dodecyl methacrylamide, and combinations thereof.

25 12. The copolymer of claim 2, wherein the first ethylenically
unsaturated monomer is selected from the group consisting of alkyl esters of acrylic acid,
methacrylic acid, mono or di-alkyl acrylamides, and mono or di-alkyl methacrylamides,
wherein the alkyl has from 2 to 8 carbon atoms; alkyl styrenes, wherein alkyl has from 4
to 8 carbons, such as t-butyl; and combinations thereof.

30 13. The copolymer of claim 2, wherein the first ethylenically
unsaturated monomer is selected from the group consisting of n-butyl acrylate, t-butyl
acrylate, ethyl acrylate, 2-hexyl acrylate, and combinations thereof.

14. The copolymer of claim 2, wherein the polyfunctional monomer has the general formula:



5

where n and m are integers from 1 to 4;

R₁, R₃ are selected from the group consisting of H and alkyl; and,

R₂ is selected from the group consisting of alkyl, cycloalkyl, aryl,

-(CH₂-CH₂-O)_p- where p = 1 to 50, -(CH₂(CH₃)-CH₂-O)_p- where p = 1 to 50,

10

amido, ester, polyamido, and polyester.

15. The copolymer of claim 2, wherein the polyfunctional monomer is selected from the group consisting of allyl methacrylate, allyl acrylate, vinyl methacrylate, vinyl acrylate, vinyl acrylamide, vinyl methacrylamide, allyl methacrylamide, allyl acrylamide, and mixtures thereof.

15

16. The copolymer of claim 2, wherein the reactivity of the first functional group is from about three to ten times more than the reactivity of the second functional group, allyl or vinyl.

20

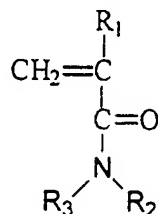
17. The copolymer of claim 2, wherein the first functional group is an allyl vinyl group and wherein the second functional group is selected from the group consisting of methacrylic and acrylic functional groups.

25

18. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is sufficiently water soluble or dispersible to form at least a 20 weight percent solution when dissolved in water.

19. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of:

1) ethylenically unsaturated amides of the general formula:



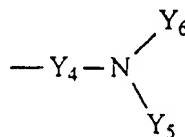
5 where R_1 is selected from the group consisting of -H, -CH₃, -CH₂-CH₃, branched or linear alkyl, aryl, and cycloalkyl;

R_2 and R_3 are selected from the group consisting of:

-H, -CH₃, -CH₂-CH₃, branched alkyl, linear alkyl, aryl, cycloalkyl;

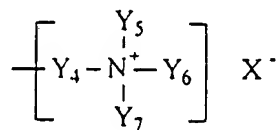
acid or salt functional groups, such as -SO₃H, -SO₃ M (where M = metal);

10 amino functional groups of the general formula:



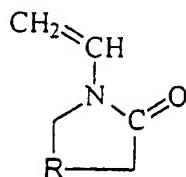
where Y_4 , Y_5 , Y_6 are -H, -CH₃, -CH₂-CH₃, branched or linear alkyl, aryl, cycloalkyl, and combinations thereof;

and quaternized amino functional groups of the general formula:



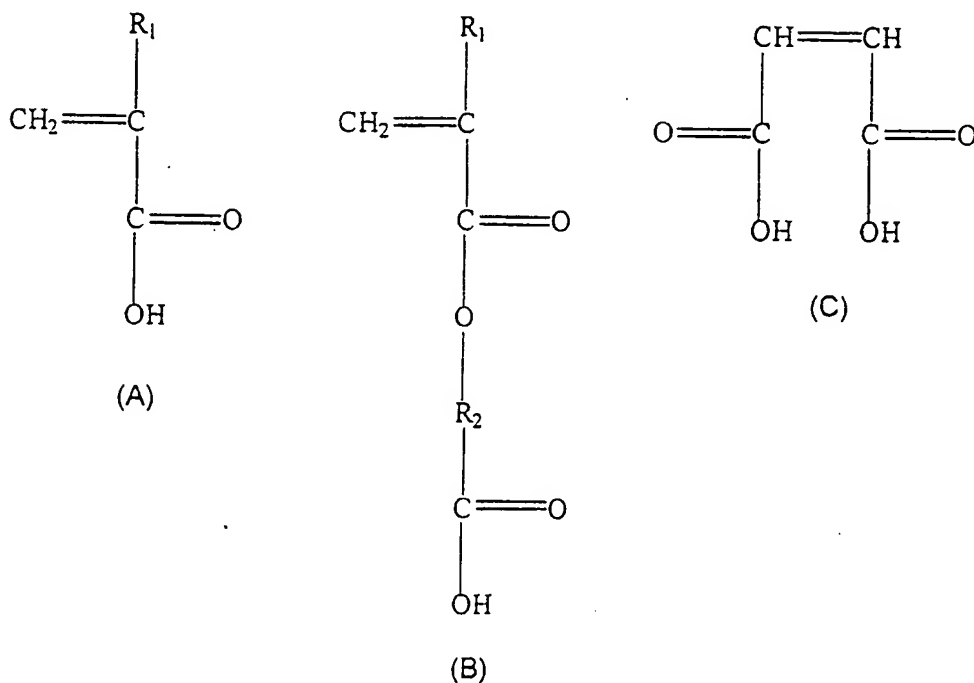
15 where Y_4 , Y_5 , Y_6 are -H, -CH₃, -CH₂-CH₃, branched or linear alkyl, aryl, cycloalkyl, and combinations thereof;

2) ethylenically unsaturated water soluble heterocyclic of the general formula:



where R is an alkylene group, such as $R_2 = -[CH_2-]_n$, where n is an integer from 1 to 4; and,

3) ethylenically unsaturated carboxylic acids of one of the three general formulae:



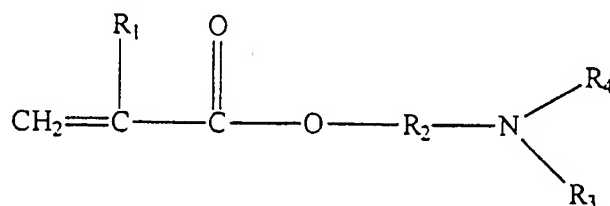
where R_1 is selected from the group consisting of -H, -CH₃, -CH₂CH₃;

R_2 is selected from the group consisting of $-[CH_2-]_n$, where n is an integer from 1 to 40; linear or branched alkyl; cycloalkyl; aryl; polyethylene oxide, such as $-(CH_2-CH_2-O)_p-$ where p = 1 to 50; and polypropylene oxide, such as $-(CH_2(CH_3)-CH_2-O)_p-$ where p = 1 to 50.

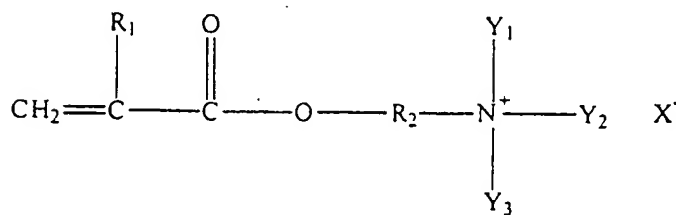
20. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is an ethylenically unsaturated amide selected from the group consisting of acrylamide, methacrylamide and fumaramide, and their N-substituted derivatives, such as 2-acrylamido-2-methylpropane sulfonic acid, N-(dimethylaminomethyl) acrylamide; N-(trimethylammonium-methyl) acrylamide chloride; and N-(trimethylammoniumpropyl)-methacrylamide chloride.

21. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is a heterocyclic amide selected from the group consisting of vinyl pyrrolidone and vinyl caprolactam.

22. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is an ethylenically unsaturated carboxylic acid selected from the group consisting of: acrylic acid; methacrylic acid; maleic acid; itaconic acid; vinylaryl sulfonic acid, salts of ethylenically unsaturated quaternary ammonium compounds, such as vinylbenzyl trimethyl ammonium chloride; sulfoalkyl esters of unsaturated carboxylic acids, and aminoalkyl esters of unsaturated carboxylic acids of the general formula:



and quaternized salts of unsaturated carboxylic acids of the general formula:



where R_1 is selected from the group consisting of -H, -CH₃, -CH₂CH₃;

R_2 is selected from the group consisting of -[CH₂]_n, where n is an integer from 1 to 40; linear alkyl; branched alkyl; cycloalkyl; aryl; polyethylene oxide, such as -(CH₂-CH₂-O)_p- where p is an integer from 1 to 50, polypropylene oxide such as -(CH₂(CH₃)-CH₂-O)_p- where p is an integer from 1 to 50; and combinations thereof;

Y_4 , Y_5 , and Y_6 are selected from the group consisting of -H, -CH₃, -CH₂-CH₃, branched or linear alkyl, aryl, cycloalkyl, and combinations thereof; and

X is an acid radical selected from the group consisting of chloride, bromide, sulfate, sulfonate, phosphate, methyl, and ethyl sulfonate.

23. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of 2-aminoethyl methacrylate; N,N-dimethyl-aminoethyl methacrylate; N,N-dimethyl aminoethyl acrylate; 2-tert-butyl aminoethyl methacrylate; 2-trimethylammonium ethylmethacrylate chloride; 2-trimethylammonium ethylacrylate chloride; vinyl amines, such as vinyl pyridine and vinyl morpholine; diallyl amines; and diallyl ammonium compounds, such as diallyl dimethyl ammonium chloride.

24. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, C₁-C₄ alkyl half esters of maleic and fumaric acids, and combinations thereof.

25. The copolymer of claim 2, wherein the polyfunctional monomer is allyl methacrylate, the first ethylenically unsaturated monomer is a mixture of n-butyl acrylate and (meth)acrylic acid and the second ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

26. A block copolymer adaptable for use in forming a hair styling composition, the copolymer having a plurality of glass transition temperatures, the copolymer including:

a hydrophobic organic polymeric block; and

hydrophilic organic block.

27. A hair styling composition including:

from about 0.01-20% by weight of a copolymer which has been prepared

utilizing:

a polyfunctional monomer having at least a first functional group and a second functional group, the reactivity of the first functional group being higher than that of the second functional group;

5 a first ethylenically unsaturated monomer which copolymerizes preferentially with the first functional group of the difunctional monomer to form a first, hydrophobic block; and

a second ethylenically unsaturated monomer which is hydrophilic and copolymerizes with the second functional group of the difunctional monomer to form a second block and a copolymer having both hydrophobic and hydrophilic blocks.

10

28. The hair styling composition of claim 27, wherein the polyfunctional monomer comprises from about 0.005 to 2 mole percent of the total monomers;

15 the first ethylenically unsaturated monomer comprises from about 30 to about 95 mole percent of the total monomers; and,

the second ethylenically unsaturated monomer comprises from about 5 to about 80 mole percent of the total monomers.

20 29. The hair styling composition of claim 27, further including at least one of the following materials:

0 to 25 weight percent of an emulsifier;

0.05 to 99% solvents;

0.05 to 10% rheology modifiers;

0.05 to 5% neutralizing agents;

25 0-60 weight percent of a liquid propellant or gas; and,

0-1% of a surfactant.

30 30. A hair styling composition including:
from about 0.5 to 99 weight percent water or water and alcohol; and
from about .01 to 20 weight percent of a block copolymer, the copolymer having a plurality of glass transition temperatures. the copolymer including:

a hydrophobic organic block; and
hydrophilic organic block joined to the hydrophobic block..

5 31. The hair styling composition of claim 30, wherein the
hydrophobic block is a polyacrylate.

 32. A method of preparing a hair styling composition, the method
including preparing a copolymer having hydrophobic and hydrophilic blocks by
copolymerizing:
10 a polyfunctional monomer having at least a first functional group and a
second functional group, the reactivity of the first functional group being higher than that
of the second functional group;

 a first ethylenically unsaturated monomer which is an ethylenically
unsaturated monomer which copolymerizes preferentially with the functional group of
15 the difunctional monomer having the higher reactivity to form a first hydrophobic block;
and

 a second ethylenically unsaturated monomer which has at least one
carboxylic acid group and copolymerizes with the second functional group to form a
copolymer having both hydrophobic and hydrophilic blocks.

20 33. The method of claim 32, wherein the preparing the copolymer
includes:

 adding to a reaction vessel, a solvent, the polyfunctional monomer or
monomers, the first ethylenically unsaturated monomer or monomers, and an initiator;

25 reacting the monomers to form a first block;

 adding a second ethylenically unsaturated monomer or monomers having
at least one carboxylic acid group; and,

 reacting the monomers to form a second block and a copolymer having
both hydrophobic and hydrophilic groups and at least two glass transition temperatures.

30 34. The method of claim 33, wherein the initiator is selected from the
group consisting of azo-type initiators and peroxy-type initiators.

35. The method of claim 34, wherein the initiator is an azo-type initiator selected from the group consisting of azobis-dimethylvaleronitrile, azobis-isobutyronitrile, azobis-methylbutyronitrile, and combinations thereof.

5

36. The method of claim 34, wherein the initiator is a peroxy-type initiator selected from the group consisting of di-T butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxy-pivalate, lauryl peroxide, cumene hydroperoxide, ethyl hexyl peroxodicarbonate, diisopropyl peroxydicarbonate, 4-(t-butylperoxyperoxy-carbonyl)-3-hexyl-6-7-(t-butylperoxycarbonyl)heptyl cyclohexene, cumene hydroperoxide and t-butyl peroxyneodecanoate, t-butyl hydroperoxide, benzoyl peroxide, and combinations thereof.

10

37. The method of claim 36, wherein the initiator is t-butyl peroxy-pivalate.

15

38. The method of claim 34, wherein the initiator is at a concentration of from about 0.005 to 1 mole percent of the total monomers.

20

39. The method of claim 33, wherein the solvent is selected from the group consisting of water, hydrocarbons, alcohols, ethers, esters, aromatic solvents, glycols, glycol ethers, glycol esters, and combinations thereof.

25

40. The method of claim 39, wherein the solvent also includes water.

41. The method of claim 39, wherein the solvent is selected from the group consisting of water, ethyl alcohol, isopropyl alcohol, t-butyl alcohol, ethyl acetate, methyl acetate, butyl acetate, benzene, toluene, methylene chloride, hexane, cyclohexane, mineral spirits, and combinations thereof.

30

42. The method of claim 39, wherein the solvent is isopropyl alcohol and water.

43. The method of claim 33, wherein the copolymer is produced in the same reaction vessel.

5 44. The method of claim 33, further including neutralizing the copolymer so that between 0.1 and 100 percent of the carboxylic acid groups are neutralized.

10 45. A method of preparing a hair styling composition, the method including:

 preparing a block copolymer, the copolymer having a plurality of glass transition temperatures, the copolymer including:

 a hydrophobic organic polymeric block; and
 hydrophilic organic block;

15 combining about 1-10 percent of the copolymer with from about 20 to 97 weight percent of water and from about 0 to 80 weight percent of an organic solvent.

 46. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of methyl acrylate, methyl
20 methacrylate, butyl acrylate, ethyl acrylate, octyl acrylate, dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, alkyl esters derived from the reactions of alkanols having from 2 to 20 carbon atoms with acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid, nonyl α -phenyl
25 acrylate, nonyl- α -phenyl methacrylate, dodecyl- α -phenyl acrylate and dodecyl- α -phenyl methacrylate, N-butyl acrylamide, T-butyl acrylamide, octyl acrylamide, N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl acrylamide, octene-1, decene-1, dodecene-1, hexadecene-1, vinyl laurate, vinyl stearate, dodecyl vinyl ether, hexadecyl vinyl ether, N-vinyl lauramide, N-vinyl stearamide, t-butyl styrene, and combinations
30 thereof.

47. The copolymer of claim 2, wherein said first block has a glass transition temperature which is less than the glass transition temperature of said second block.

5 48. The copolymer of claim 2, wherein the polyfunctional monomer has a fast reacting unsaturated group of the acrylate or methacrylate type and a slower reacting group of the allyl type.

49. The copolymer of claim 2, wherein said polyfunctional monomer is allyl methacrylate.

10 50. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a blend of hydrophobic and hydrophilic monomers.

15 51. The copolymer of claim 2, wherein the second ethylenically unsaturated monomers are a blend of hydrophilic, ionizable monomers.

52. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid.

20 53. The copolymer of claim 52, wherein said acid monomer comprises 50 mole % or less of said monomer mixture.

54. The copolymer of claim 2, wherein the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid.

25 55. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid, the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid, and the acid monomers comprise about 50 to about 70 mole % of the total monomers.

30 56. The copolymer of claim 2, wherein said first block has a glass transition temperature of about 30 °C or less and said second block has a glass transition temperature of greater than 30 °C.

57. The copolymer of claim 2, wherein said first block has a glass transition temperature of about 0 °C or less and said second block has a glass transition temperature of greater than 0 °C.

5

58. The copolymer of claim 50, wherein said hydrophilic monomer comprises 60% by weight or less of the blend of hydrophobic and hydrophilic monomers.

10

59. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid, the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid, and the acid monomers comprise about 50 to about 50 mole % of the total monomers.

15

60. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of vinylbenzyl sulfonic acid, vinylbenzyl trimethyl ammonium chloride, and 2-sulfoethyl methacrylate.

INTERNATIONAL SEARCH REPORT

In .tional Application No

PCT/US 99/30790

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F265/04 C08F291/00 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 484 053 A (GOLDSCHMIDT AG TH) 24 August 1977 (1977-08-24) examples ---	1-3, 8-10, 12-18, 22,24, 25,46-55
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X	US 5 403 894 A (TSAI MIN-CHI ET AL) 4 April 1995 (1995-04-04) column 4, line 3 -column 5, line 62; examples --- -/--	1-19

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

22 May 2000

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30790

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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